MINISTERIO DE CIENCIA E INNOVACIÓN

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

Modelling the continuous calcination of $CaCO_3$ under CFB oxy-fuel conditions

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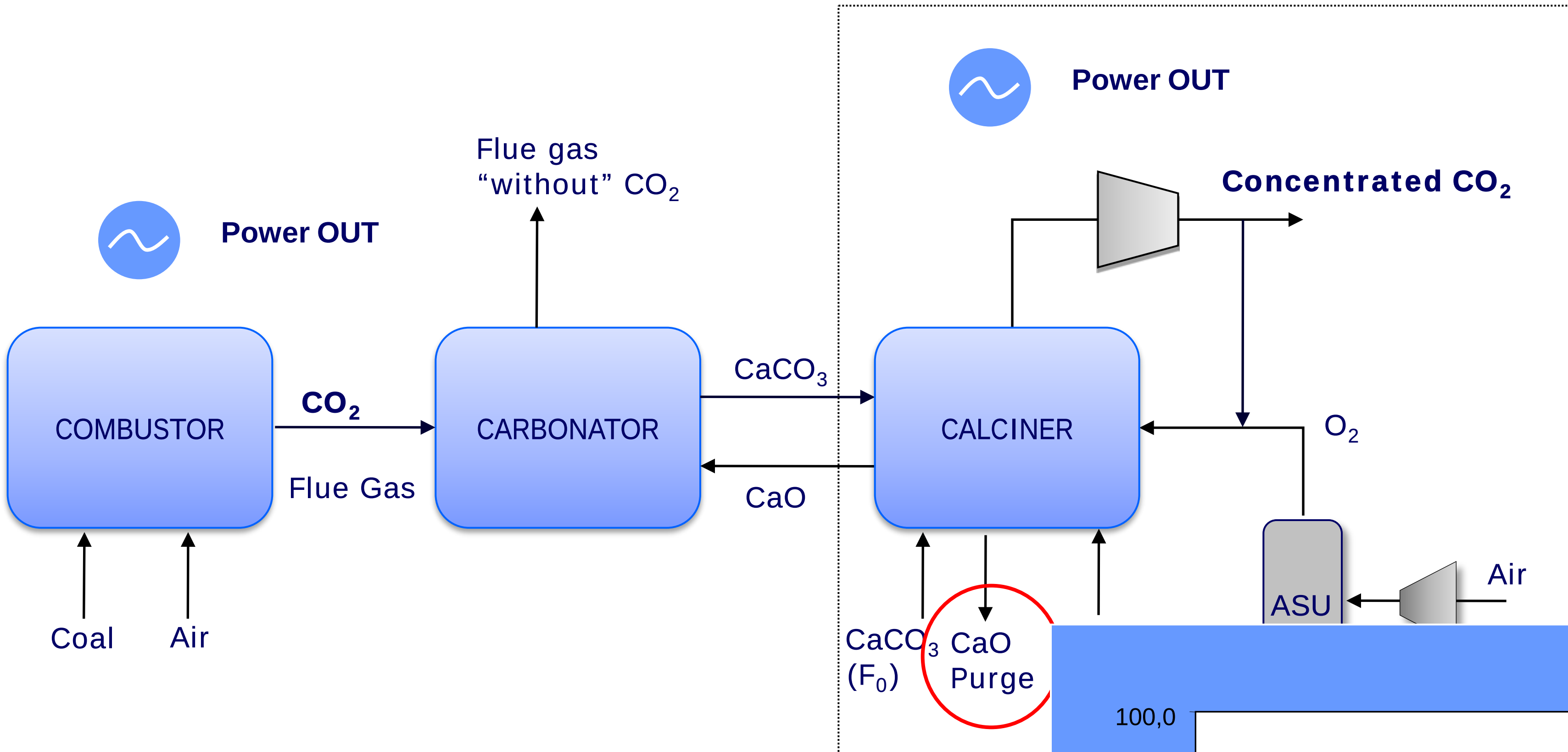
Workshop on CFB oxycombustion

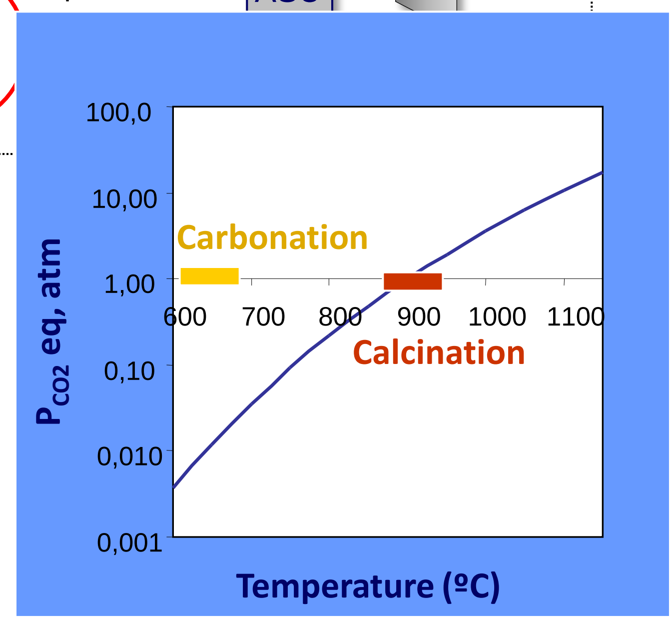
27-28 of June, Ottawa, Canada

Modeling the continuous calcination of $CaCO_3$ under CFB oxy-fuel combustion

- **Motivation of this work**
  - **Ca-looping for post-combustion CO_2 capture with Oxy-fired CFB calciner**
- **Preliminar modelling work of calciner:**
  - **Particle model**
  - **Reactor model**

Postcombustion Ca-looping





Some advantages of Ca-looping:

- **Low energy penalty**
- **Purge of CaO: synergies with cement industry**
- **Pre-treatment of flue gas no needed (SO_2 co-capture)**

Next steps in Ca-looping development: 1.7 MWt pilot plant

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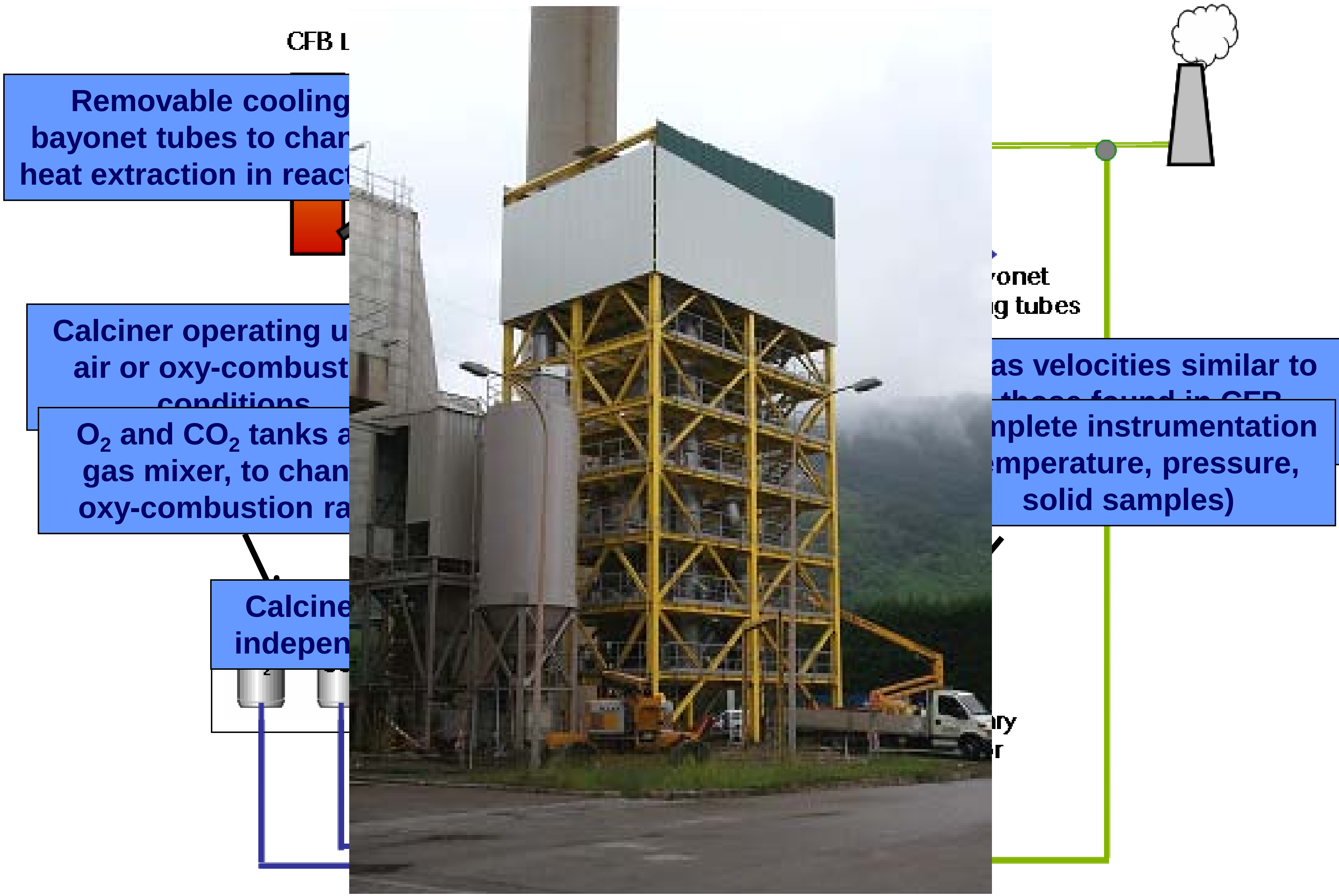


FP7 “CaOling” Project:
Development of postcombustion CO2 capture with CaO in a large testing facility:
www.caoling.eu

Main objective:

To advance in the experimental validation of the carbonate looping cycle (at a 1.7 MWt scale range) and demonstrate that this is a low cost, highly energy efficient CO_2 capture technology, suitable for retrofitting coal combustion power plants

Operation will start in September 2011

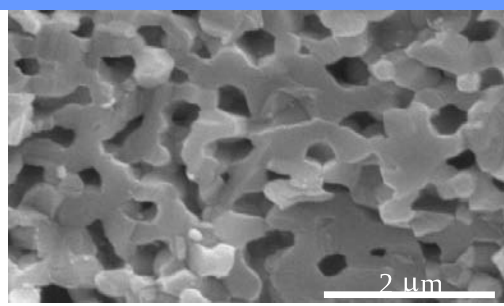
- Motivation of this work
  - Ca-looping for post-combustion CO2 capture: description of the process
  - Status of the technology

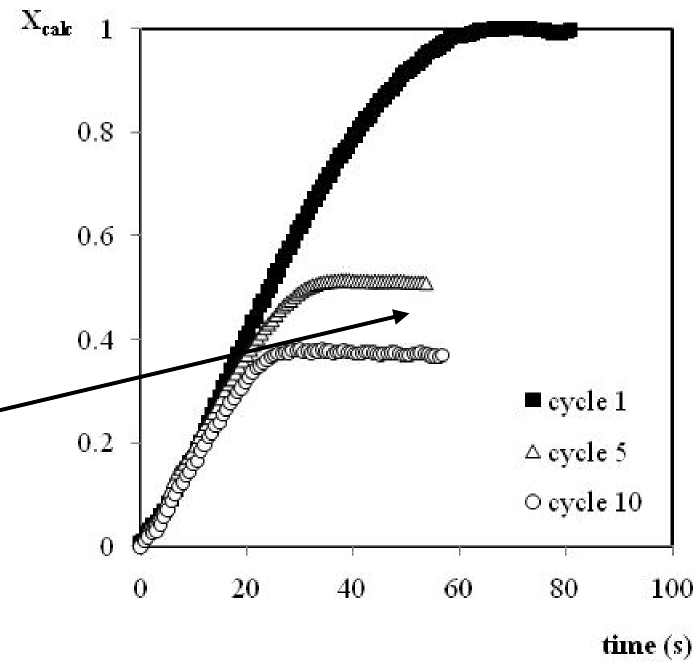
- **Preliminar modelling of the calciner:**
  - **Particle model of highly cycled CaO particles**
  - **Reactor model**

Particle calcination model

For typical Ca-looping particles (average d_p ~ 90 µm and open pore structures):

<u>homogeneus reaction models at particle level</u>





Compostilla Limestone (NW Spain)

$$\frac{dX_{calci}}{dt} = k_c \cdot (1 - X_{calci})^{2/3} \cdot (C_{eq} - C_{CO2})$$

Fang et al *E&F 2009*

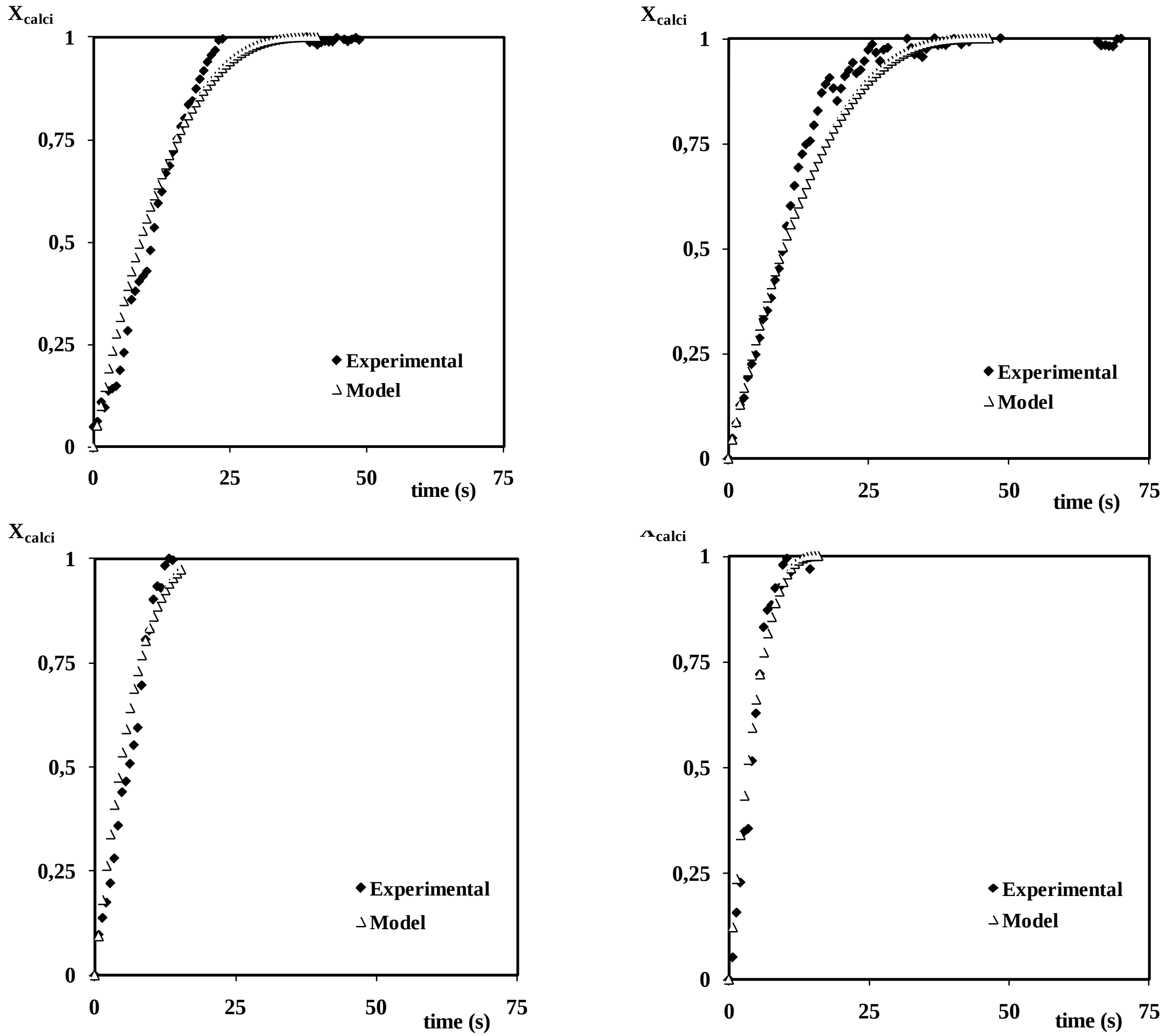
+

$$X_{calci,N} = \frac{moles\ of\ CO_2\ released}{moles\ of\ CaO \cdot X_{N-1}}$$

$$X_N = \frac{1}{k \cdot N + \frac{1}{(1 - X_r)}} + X_r$$

Grasa et al *I&EC 2006*

Particle calcination model vs TG experimental data



Compostilla Limestone (NW Spain) dp 75-125 micron, cycle 5 (left) and 10 (right) at 910ºC: (top) 75 kPa of CO_2 partial pressure, (bottom) 25 kPa of CO_2 partial pressure

I. Martínez, G. Grasa, R. Murillo, J.C. Abanades. Kinetic of calcination of cycled sorbent particcles in a Ca-looping system. *Energy and Fuels* 2011 (submitted July 2011)

- Motivation of this work
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- **Preliminar modelling of the calciner:**
  - **Particle model**
  - Reactor model

Initial assumptions for calciner reactor:

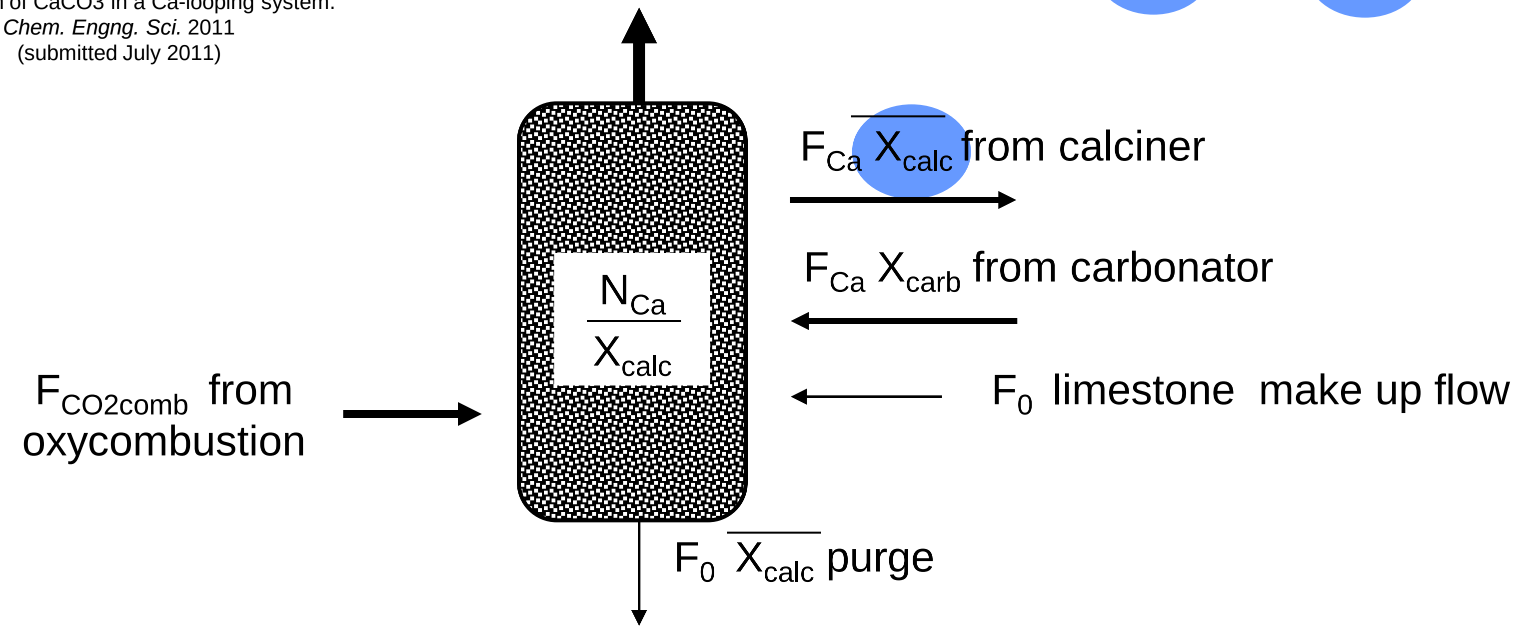
• Instantaneous and perfect mixing of the solids (known inventory of material N_{CaO} , solid circulation rate F_{CaO} and make up flow F_0)

• Plug flow for the gas phase

Modelling the continuous calcination of $CaCO_3$

I. Martínez, G. Grasa, R. Murillo, J.C. Abanades. Modelling the continuous calcination of CaCO3 in a Ca-looping system. *Chem. Engng. Sci.* 2011 (submitted July 2011)

$$F_{CO2} = F_{CO2comb} + F_{Ca}(X_{carb} - \overline{X_{calc}}) + F_0(1 - \overline{X_{calc}})$$



Time for total calcination

$$t^* = \frac{3}{k_c \cdot (C_{eq} - C_{CO2})}$$

Average solid residence time

$$\tau = \frac{N_{Ca}}{F_0 + F_{Ca}}$$

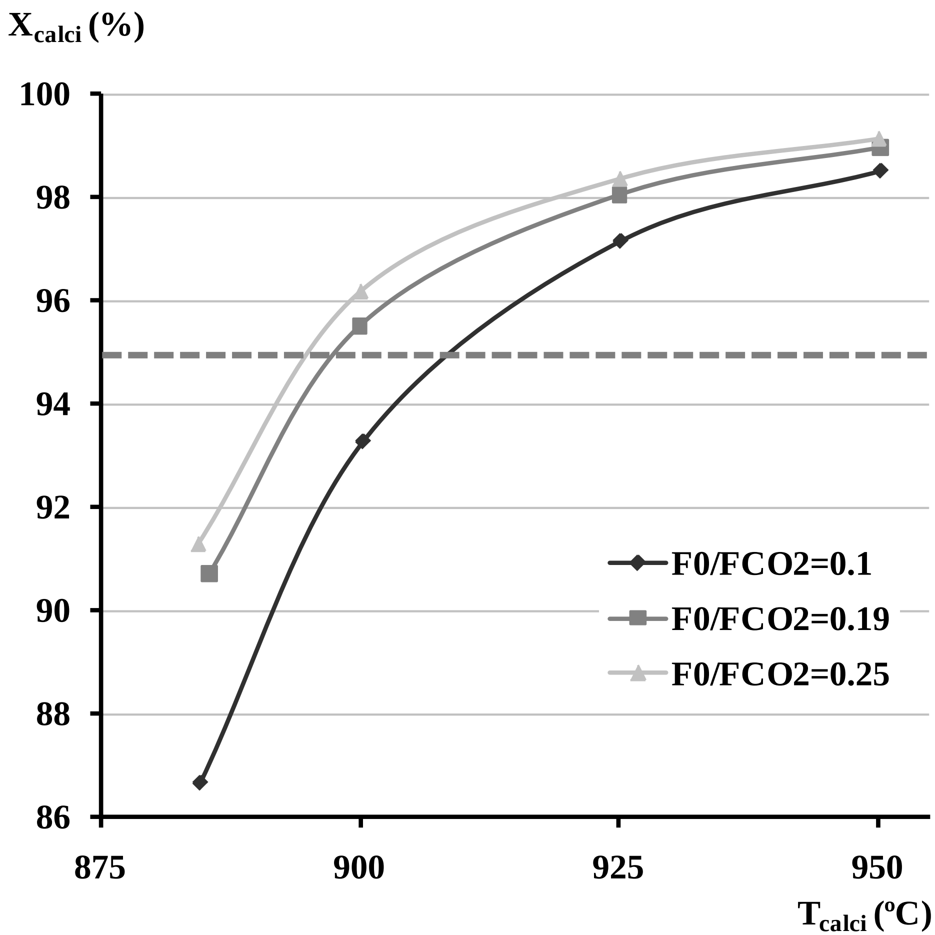
Fraction of particles not totally calcined

$$f_{calc} = 1 - \exp\left(-t^* / \tau\right)$$

Average calcination conversion

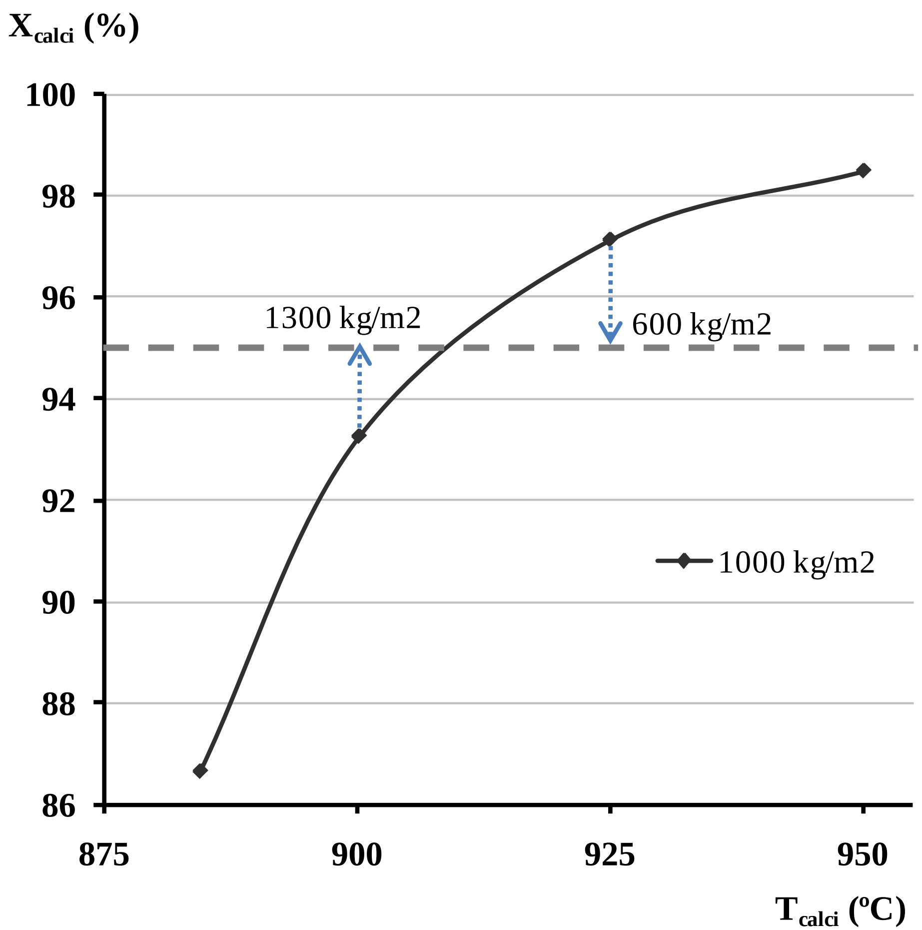
$$\overline{X}_{calc} = f_{calc} \cdot \overline{X}_{t \le t^*} + (1 - f_{calc})$$

Modelling the continuous calcination of $CaCO_3$



Average calcination conversion achieved for a solid inventory of 1000 kg/m2, for different calcination temperatures and modifying the ratio F0/FCO2 make up. PCO2=0.7 atm

Modelling the continuous calcination of $CaCO_3$



Average calcination conversion achieved for a solid inventory of 1000 kg/m2, for different calcination temperatures and effect of two different inventories. PCO2=0.7 atm, F0/FCO2=0.1

Conclusions/Remarks

- Postcombustion Calcium Looping is a rapidly developing technology, successfully characterized at small pilot plant scale, at least in Canada, Spain and Germany .
- An experimental facility has been built in La Pereda Power Plant (Spain) aiming to validate Calcium Looping technology in the 1.7 MWs size (entering operation in September 2011).

- Calcination of particles in the calciner of a Ca-looping system is facilitated by small particle sizes, low carbonate conversions and open pore structures
- A simple reactor model for calcination (CSTR for solids and PF for gas), integrating available kinetic experimental data, anticipates very high calcination efficiencies (>95%) at temperatures between 900-920ºC with bed inventories around 1000 kg/m^2

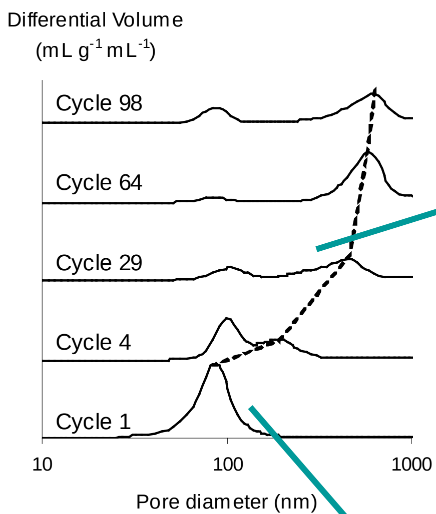
- The imminent validation of results in oxy-CFB reactors coupled with a CFB carbonator at the MW scale, will be a major step in the development and scaling up of Ca-looping technology for postcombustion CO_2 capture.

Extras (por si acaso)

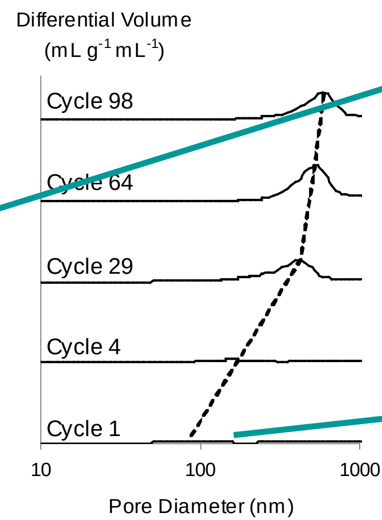
Textural evolution of CaO during cycling

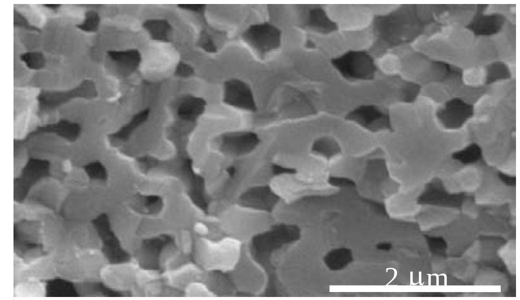
Pore size evolution

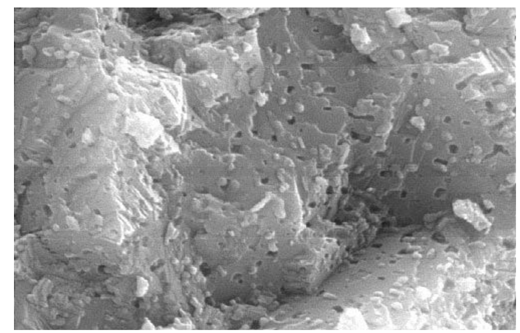
Calcined

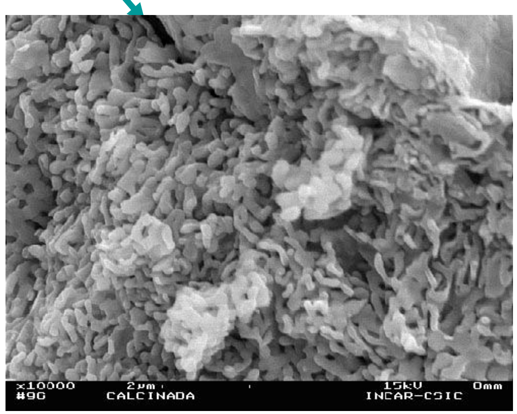


Carbonated









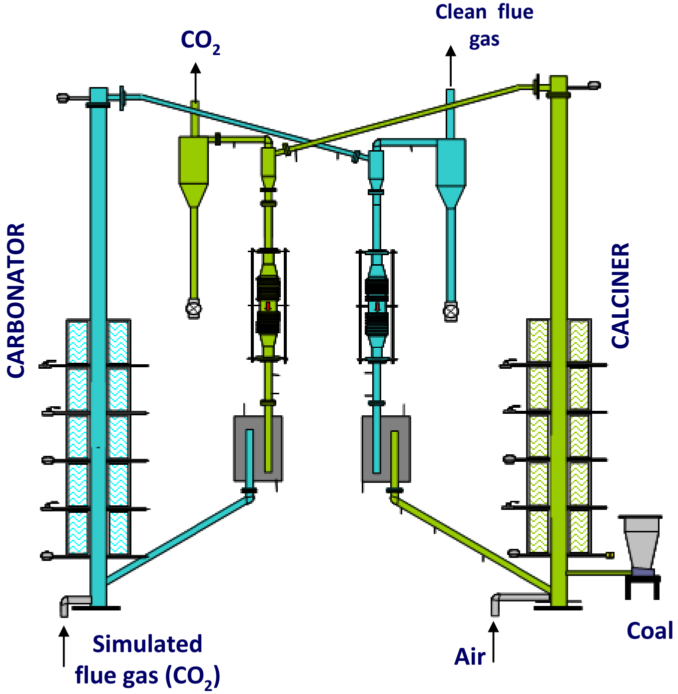
D. Alvarez, J. Carlos Abanades, Determination of the critical product layer thickness in the reaction of CaO with CO2 *Ind. Eng. Chem. Res,* 5608-5615, **2005**

Pore size and shape effect on the recarbonation performance of calcium oxide submitted to repeated calcination/recarbonation cycles.
D. Alvarez, JC Abanades, *Energy and Fuels* 19, 270-278 **2005**

Small pilot-plant facility: Description

Small pilot plant at INCAR-CSIC (30 kWt)

Two interconected circulating fluidized beds



Main features:

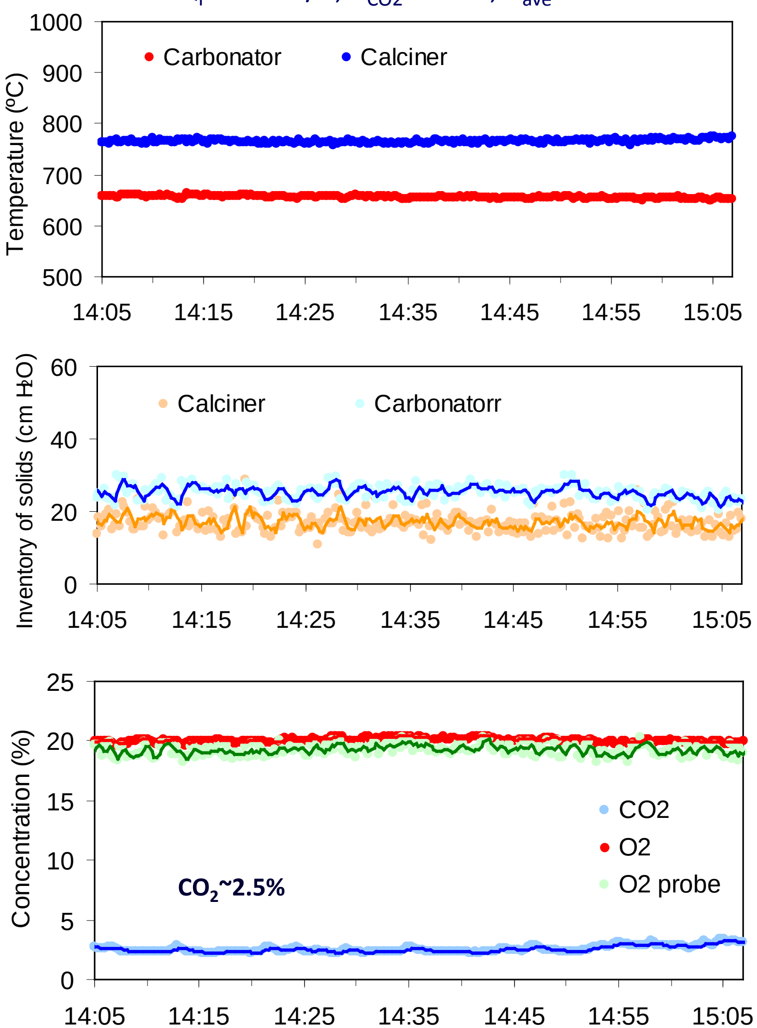
- Two CFB reactors (Height~6.5 m, diameter=100 mm)
- Electrically heated
- Measurement port (temperature, pressure, gas composition)
- Solid circulation measurements
- Solid samples characterization (TG analysis, C/S analyzer)

Small pilot-plant facility: Experimental results

Steady state:

Defined as the situation where carbonator and calciner temperature, pressure drops, inlet gas flows and outlet gas concentration remain constant for a period of time of at least 10-20 minutes.

Q_T= 19 m^3/h, ν_{CO2} = 0.12, X_{ave}= 0.08



Ref: *Rodriguez et al. AIChE J 2011, 57 (5) 1356-1366*

Some measured experimental parameters:

- Average carbonation temperature
- Inventory of solids
- Inlet CO_2 concentration and total flow
- Outlet CO_2 concentration
- Carbonate content of entering and exiting solids
- Average CO_2 carrying capacity of solids
- Solid circulation rates

Main achievements:

- Has completed 450 h of operation
- Max. CO_2 capture efficiency: 97 %
- Absorption capacity up to 7 molCO_2/m^2s)

Post-combustion CO2 capture using carbonate looping

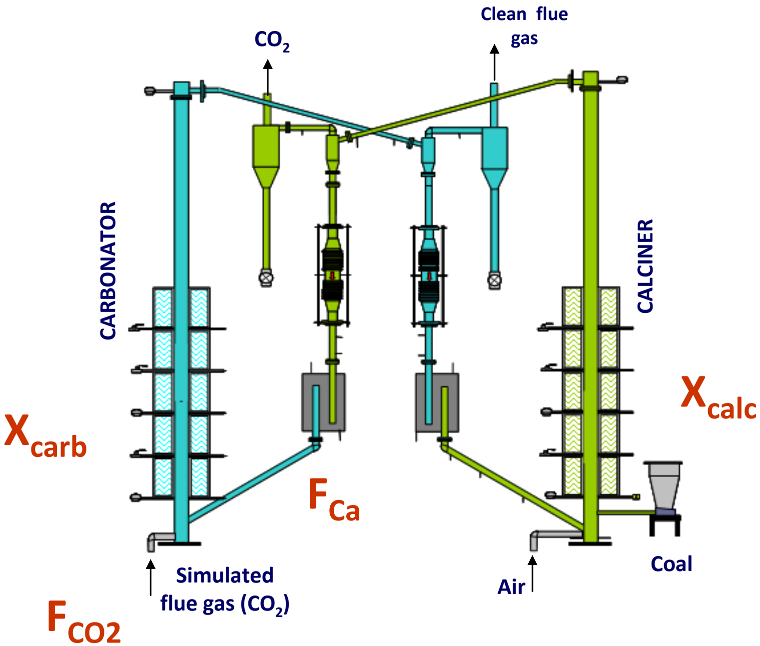
CO_2 mass balance in the system

CO_2 reacting with CaO in the bed **=** CO_2 removed from the gas phase **=** $CaCO_3$ formed in the circulating stream of CaO

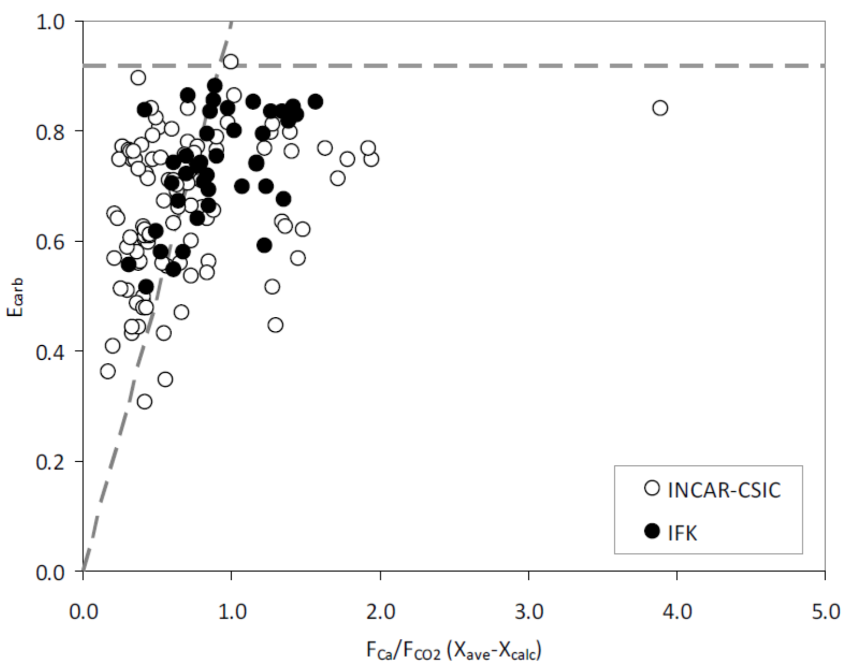
$$\left(\begin{array}{l}\text{CaCO}_3 \text{ formed in the} \\ \text{circulating stream of CaO}\end{array}\right) = F_{Ca}\left(X_{carb} - X_{calc}\right)$$

$$F_{CO_2}\, E_{carb} \leq F_{Ca}\left(X_{ave} - X_{calc}\right)$$

Experimental measurement

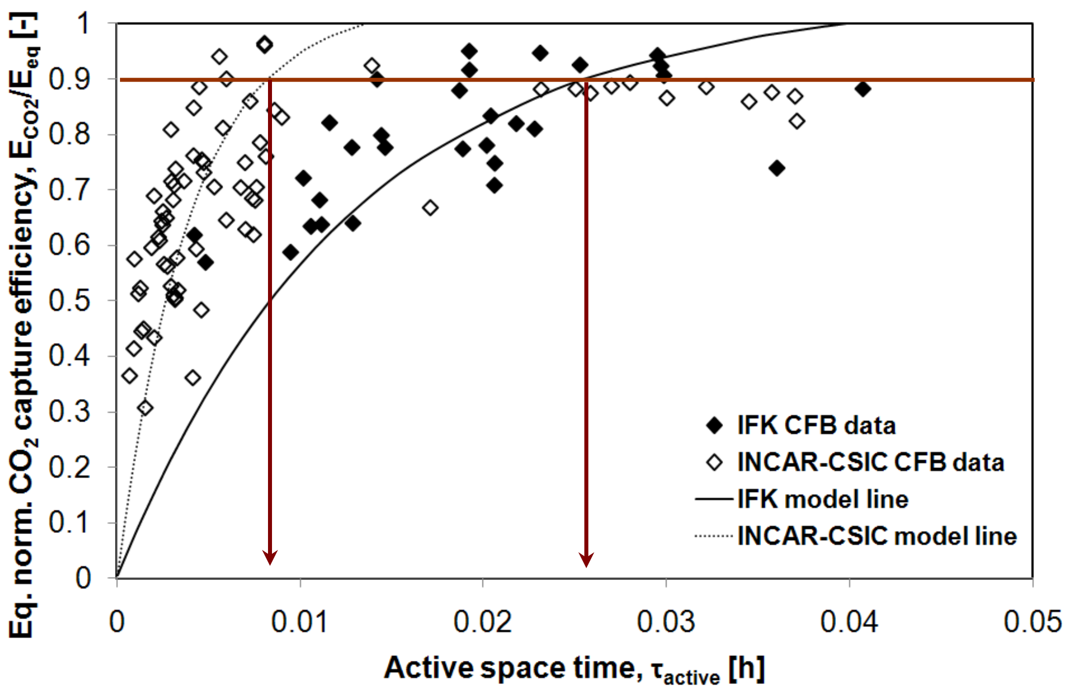


Supply of active flow of CaO



Ref: *Rodriguez et al. Energy Procedia 2011, (4) 393-401*

Model validation in two experimental facilities: IFK and CSIC



$$E_{carb} = \frac{N_{Ca}\, f_a\, \varphi\, k_s\, X_{ave}\left(\overline{f_{CO2} - f_e}\right)}{F_{CO2}} = \tau_{active}\, \varphi\, k_s \left(\overline{f_{CO2} - f_e}\right)$$

Active space time

$$\tau_{active} = \frac{N_{CaO}}{F_{CO2}} f_a X_{ave}$$

Critical active space time at which

E_{CO2}/E_{eq}>90%:

Experimental data:

Inlet CO_2 Vol. % = 11.4 for IFK &16.5 for INCAR-CSIC

T_{carb}= 634-660 °C, $X_{max,ave}$= 0.08-0.23

Main differences between both series of experimental and calculated data

- Different inlet CO2 concentration (11.4% IFK, 16.5% INCAR)
- Different limestone (IFK limestone less reactive, k_s=0.20s^{-1})

Ref: *Charitos et al. Ind. Eng. Chem. Res. Submitted for publication. Common paper between IFK and INCAR-CSIC*